

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

AN X-RAY FLUORESCENCE SPECTROMETER AND ITS
APPLICATIONS IN MATERIALS STUDIES

JAG J. SINGH AND K. S. HAN

AUGUST 1977

(NASA-TM-74062) AN X-RAY FLUORESCENCE
SPECTROMETER AND ITS APPLICATIONS IN
MATERIALS STUDIES (NASA) 18 P HC A02/MF A01
CSCL 18H

N77-30921

G3/72 42061
Unclas



National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia 23665



AN X-RAY FLUORESCENCE SPECTROMETER AND ITS
APPLICATIONS IN MATERIALS STUDIES

By Jag J. Singh and K. S. Han*
Langley Research Center

ORIGINAL PAGE IS
OF POOR QUALITY

ABSTRACT

An X-ray fluorescence spectrometer based on a Co^{57} γ -ray source has been developed for verification of the atomic percentages of iron atoms implanted in titanium fatigue targets. The iron ions were implanted in a 100 mm^2 area centered at the middle of the titanium targets to provide a 126 nm deep uniform profile containing 1, 5, and 8 a/o iron atoms. The implantation regions of the targets were bombarded with collimated Co^{57} γ -rays and the elemental characteristic X-rays detected with a 30 mm^2 , 3 mm deep Si(Li) detector. The total system resolution (detector + electronics) was $\leq 250 \text{ eV}$. Measured relative intensities of $\text{Fe}(k_{\alpha} + k_{\beta})$ and $\text{Ti}(k_{\alpha} + k_{\beta})$ X-rays from Fe-Ti targets have been compared with the values computed using fluorescent yield data reported in the literature. The computed and the measured values of $R = \text{Fe}(k_{\alpha} + k_{\beta})/\text{Ti}(k_{\alpha} + k_{\beta})$ at the three iron concentrations are in agreement, within experimental errors, as seen below: $R(1 \text{ a/o}) = 2.78 \times 10^{-4}$ (3×10^{-4}), $R(5 \text{ a/o}) = 1.38 \times 10^{-3}$ (1.5×10^{-3}), $R(8 \text{ a/o}) = 2.22 \times 10^{-3}$ (2.6×10^{-3}). The experimental values, given in parentheses, have an estimated error of $\pm 25\%$.

*Permanent address: Department of Physical Science, Hampton Institute, Hampton, VA.

INTRODUCTION

Current interest in hypersonic vehicles has aroused a great deal of interest in the fatigue damage characteristics of titanium metal and its alloys. Recently, a study of fatigue damage mechanisms in titanium metal using Fe^{57} Mossbauer spectrometry^{1,2} has been initiated. High purity (99.9%) iron ions were implanted in the high stress zone of the titanium fatigue targets. It was anticipated that the fatigue induced atomic changes in the region of iron implantation would affect Mossbauer parameters of iron atoms.^{1,2} A measurement of such changes could then be used to infer the changes in the iron atomic environments. Before the Mossbauer measurements of the iron implanted titanium targets could be started, it was felt desirable to confirm the iron atom concentration in the titanium substrate. An X-ray fluorescence technique³ was considered to be the most appropriate * nondestructive technique for this purpose. Since a 25 millicuries Co^{57} Mossbauer source was already available, it was decided to develop an X-ray fluorescence system (XRF system) based on the Co^{57} γ -rays as the exciter radiation. The XRF system, its performance and the results on ion-implanted titanium targets are described in the following pages.

X-RAY FLUORESCENCE SYSTEM

The XRF system consists of three major components: An exciter radioactive source, target holder, and X-radiation detection system. Figure 1 shows a schematic diagram of the system. A well-collimated beam of the Co^{57} γ -rays is

*This conclusion was dictated by the fact that the FeTi targets should not be modified in any way, either by heating under charged particle bombardment or by impurity contamination if the targets are placed in a vacuum.

allowed to fall on the (Fe-Ti) target. The target is positioned so that the exciter beam covers the entire implantation zone. The target atoms get excited under γ -bombardment and then de-excite by emitting their characteristic radiations. These characteristic X-rays are detected with a 30 mm^2 , 3-mm-thick Si(Li) detector with an 8.5- μm -thick Be window. The Si(Li) detector output, after amplification, is analyzed using a 400-channel pulse height analyzer. Figures 2 and 3 show typical X-ray spectrum from Ti and Fe targets. The total system resolution (FWHM) is calculated to be 250 eV. The Si(Li) detector resolution has been quoted at 185 eV (5.9 keV/1000 cps) by the manufacturer.

FE-TI TARGET PREPARATION

The Ti targets were fabricated in the form shown in figure 4. This target geometry was selected because of the availability of extensive fatigue damage data in targets of this configuration.⁴ The Fe^+ ions were implanted in a 100 mm^2 circle centered at the elox cut in the middle of the titanium target. The ion implantation accelerator available could operate reliably only in the range 10-300 keV. It was therefore decided to implant Fe atoms^{*} in Ti uniformly up to a thickness of 126 nm, which is the projected range⁵ of 275 keV Fe^+ ions in Ti. Table I lists the various Fe^+ ion energies and the corresponding implantation doses (ions/cm^2) to provide flat 1, 5, and 8 atomic percent of Fe atoms profiles in 126 nm deep layer in titanium.

*The Fe^+ ions were implanted by KSW Electronics Corporation, Burlington, MA, under contract to NASA Langley Research Center.

Table I.- Fe⁺-ion energies and implantation doses for a flat 126 nm deep profile

No.	Fe ⁺ Energy (keV)	Implantation Dose (ions/cm ²)		
		1 a/o	5 a/o	8 a/o
1	16	3.48 x 10 ¹⁴	1.74 x 10 ¹⁵	2.78 x 10 ¹⁵
2	33	5.46 x 10 ¹⁴	2.73 x 10 ¹⁵	4.37 x 10 ¹⁵
3	63	9.10 x 10 ¹⁴	4.53 x 10 ¹⁵	7.25 x 10 ¹⁵
4	111	1.47 x 10 ¹⁵	7.35 x 10 ¹⁵	1.18 x 10 ¹⁶
5	180	1.72 x 10 ¹⁵	8.61 x 10 ¹⁵	1.38 x 10 ¹⁶
6	275	4.89 x 10 ¹⁵	2.45 x 10 ¹⁶	3.91 x 10 ¹⁶

CALCULATIONS OF RELATIVE CONCENTRATION OF FE AND TI

ATOMS ON THE BASIS OF MEASURED FE AND TI

CHARACTERISTIC X-RAY INTENSITIES

For the purpose of calculations, the 126 nm deep ion-implanted region will be divided into six parallel strips. Both the Ti and Fe k-X-rays will have to pass through all the overlying strips before escaping from the target. Since the Ti X-rays cannot escape the target if they have to penetrate through more than 126 μm of Ti,^{*} the effective thickness of the Ti substrate

*This is easily seen from the following equation:

$$\begin{aligned}
 I(126 \mu\text{m}) &= I_0 e^{-\mu(4.5 \text{ keV}) \times 0.0126} \\
 &= I_0 (0.0017)
 \end{aligned}$$

would be considered to be 126 μm , even though the nominal substrate thickness is 1500 μm . The effective Ti thickness would be subdivided into 30 parallel strips for the purpose of calculating attenuation suffered by Ti X-rays starting from various sublayers. Figure 5 shows the proposed calculational model detailed in Appendix 1.

For illustrative purposes, calculations will be made for the target having 8 percent Fe implanted in Ti. The relevant information about the X-rays of interest are listed below:^{6(c)}

X-Ray Energy	Absorption Coefficient (cm^2/gm)	
	Ti	Fe
4.51 keV (Ti- k_α)	111.4	188.3
4.93 keV (Ti- k_β)	86.8	146.9
6.40 keV (Fe- k_α)	370.1	70.4
7.06 keV (Fe- k_β)	285.7	53.3

For calculating attenuation through the implantation zone, it will be assumed that:

$$\frac{\mu}{\rho}(\text{mixture}) = \frac{\mu_1}{\rho_1} w_1 + \frac{\mu_2}{\rho_2} w_2 \quad (1)$$

where $\mu_{1,2}$ and $\rho_{1,2}$ are the attenuation coefficients (cm^{-1}) and the densities (gms/cc), respectively, and w_1 and w_2 are weight fractions of the constituents in the implantation zone. The following values of the attenuation coefficients are thus calculated for the implantation zone:

$$4.51 \text{ keV} \rightarrow 544.9 \text{ cm}^{-1}; 4.93 \text{ keV} \rightarrow 424.6 \text{ cm}^{-1}$$

$$6.40 \text{ keV} \rightarrow 1575.3 \text{ cm}^{-1}; 7.06 \text{ keV} \rightarrow 1215.6 \text{ cm}^{-1}$$

Using these values, it is calculated that 99.0 percent of the $\text{Fe}(k_\alpha)$ and 99.7 percent of the $\text{Ti}(k_\alpha)$ X-rays will pass through the implantation zone. Similar calculations show that 15.5 percent of all the Ti k-X-rays produced in the 126 μm "effective" Ti substrate will pass through it.

Extensive theoretical and experimental data compilations have been published⁶ on the γ -ray attenuation coefficients in various elements. This data has been used to calculate the efficiency for characteristic X-ray production in Ti and Fe targets under Co^{57} radiation* bombardment. The review paper of Bambynek et al.^{3(d)} has been used as the source for fluorescent yield data to compute the k-X-ray production in Ti and Fe elements. Using these sets of data, the following relative intensities of the Ti and Fe k-X-rays are estimated:

$$\text{Fe}(k_\alpha + k_\beta) \simeq \text{const} \times (4.75 \times 10^{-3}) \quad (2)$$

$$\text{Ti}(k_\alpha + k_\beta) \simeq \text{const} \times (2.14) \quad (3)$$

i.e.,

$$\frac{I[\text{Fe}(k_\alpha + k_\beta)]}{I[\text{Ti}(k_\alpha + k_\beta)]} = R \simeq 2.22 \times 10^{-3} \quad (4)$$

*The Co^{57} source was covered with a 178 μm aluminum absorber to remove Fe^{57} ($k_\alpha + k_\beta$) X-rays from the incident radiation. The remaining radiations (γ -rays of energies 14.4 keV, 122 keV, and 137 keV) are effective in producing characteristic X-rays in both Ti and Fe targets.

The measured value of R for 8 percent Fe-Ti target was 2.6×10^{-3} ($\pm 25\%$).

Table II lists the measured and calculated values of R for the three targets assayed.

Table II.- Comparison between the measured and calculated value of R for the three (Fe-Ti) targets

No.	Fe - percentage	R (calculated)	R (measured)
1	1 a/o	2.78×10^{-4}	3.0×10^{-4}
2	5 a/o	1.38×10^{-3}	1.5×10^{-3}
3	8 a/o	2.22×10^{-3}	2.6×10^{-3}

The calculated and the measured values are in agreement, within the experimental errors.

RESULTS AND DISCUSSION

The XRF system described has been used to experimentally verify the iron content in the three Fe-Ti targets described earlier. Each Fe-Ti target was subjected to the Co^{57} exciter radiation for a period up to 48 hours and the resultant Fe and Ti X-ray spectra were accumulated. A typical spectrum is shown in figure 6. From such spectra, the intensities of $\text{Fe}(k_{\alpha} + k_{\beta})$ and $\text{Ti}(k_{\alpha} + k_{\beta})$ X-rays were determined. The ratio of these intensities are related to the Fe atomic percentage in Ti as described earlier. Measured relative intensities of $\text{Fe}(k_{\alpha} + k_{\beta})$ and $\text{Ti}(k_{\alpha} + k_{\beta})$ X-rays from Fe-Ti targets have been compared with the values computed using fluorescence yield data

reported in the literature. The computed and measured values of

$$R = \frac{\text{Fe}(k_{\alpha} + k_{\beta})}{\text{Ti}(k_{\alpha} + k_{\beta})}$$
 at the three iron concentrations are in agreement, within

experimental errors, as seen below: $R(1 \text{ a/o}) = 2.78 \times 10^{-4}$ (3×10^{-4}),

$R(5 \text{ a/o}) = 1.38 \times 10^{-3}$ (1.5×10^{-3}), $R(8 \text{ a/o}) = 2.22 \times 10^{-3}$ (2.6×10^{-3}).

The experimental values, given in parentheses, have an estimated error of +25%.

CONCLUDING REMARKS

An X-ray fluorescence spectrometer, based on Co^{57} γ -ray source, has been developed. The system has been used to measure the atomic percentages of iron implanted in titanium targets. Measured relative intensities of $\text{Fe}(k_{\alpha} + k_{\beta})$ and $\text{Ti}(k_{\alpha} + k_{\beta})$ X-rays from Fe-Ti targets are in agreement, within experimental errors, with the calculated values based on appropriate interaction cross sections of Co^{57} gamma rays with Ti and Fe atoms.

REFERENCES

1. Jag J. Singh: (a) NASA TMX-72810 (1975).
 (b) Bull. Am. Phys. Soc., 21, 21, 1976.

2. Jag J. Singh: Nucl. Instr. and Meth., 134, 363, 1976.

3. (a) E. P. Bertin: Principles and Practice of X-Ray Spectrometric Analysis (Plenum Press, 1970).
 (b) T. J. Kneip and G. R. Laurer: Anal. Chem., 44 (No. 14), Dec. 1972.
 (c) J. R. Rhodes et al: ISA Transactions, Vol. 11, 337, 1972.
 (d) W. Bambynek et al: Rev. Mod. Phys., 44, 716, 1972.
 (e) R. Woldseth: X-Ray Energy Spectrometry (Kevex Corp., 1973).
 (f) F. S. Goulding et al: Nucl. Instr. and Meth., 142, 323, 1977.

4. Jag J. Singh and W. T. Davis:
 (a) Proceedings of 20th International Instrumentation Symp., (Albuquerque, NM, 1974) ISA-ASI 74220 (67-78), 1974.
 (b) NASA TN D-7695 (1974).

5. (a) Ward Whaling: Encyclopedia of Physics, 34, 193, 1958.
 (b) J. Lindhard, M. Scharff, and H. E. Schiott: Mat. Fys. Medd. Dan. Vid Selskab, 33, (No. 14) 1963.
 (c) W. H. Barkas and M. J. Berger: NASA SP-3013, 1964.

6. (a) G. W. Grodstein: NBS Circular # 583, 1957.
 (b) R. T. McGinnies: NBS Circular # 583 (Supplement), 1959.
 (c) W. H. McMaster et al: UCRL - 50174 (Section IV), 1969.

APPENDIX 1

METHOD OF CALCULATING RELATIVE INTENSITIES

OF IRON AND TITANIUM K-X-RAYS

For the purpose of calculating relative iron and titanium k-X-ray intensities, the Fe-Ti targets have been assumed to be titanium slabs of thickness 126 μm with a top implantation layer of thickness 126 nm. The incident Co^{57} radiation, after passing through a 178 μm thick aluminum foil has the following spectrum:

Gamma Ray Energy	No. of Gamma Rays/100 Disintegrations
137 keV	11
122 keV	88
14.4 keV	7

For calculating the intensity of Ti K-X-rays, the 126 μm thick titanium slab has been subdivided into 30 layers, each 4200 nm thick. The incident radiation at the n th layer has been calculated as follows:

$$I_{n,\gamma_i} = I_{o,i} e^{-\mu_i [0.00042(n-1)]} \quad (1)$$

where $I_{o,i}$ represents the intensity of the respective gamma ray in the incident spectrum, μ_i (in units of cm^{-1}) equals total attenuation coefficient for the i th gamma component (14.4 keV, 122 keV, or 137 keV radiation). The number of target atoms excited in the n th layer, N_n (excited), has been calculated as follows:

$$N_n(\text{excited}) = \sum_i N_t \sigma_i I_{n,\gamma_i} \quad (2)$$

where N_t = number of target atoms/cm²

σ_i = photoelectric cross section of the ith radiation

I_{n,γ_i} = number of ith radiation photons per cm².

Only the photoelectric cross sections of the radiations arriving at the nth layer have been considered in calculating the Ti k-X-ray intensity in that layer. A fluorescence yield, $w_k = 0.219$ has been assumed for titanium.^{3(d)} The nth layer Ti k-X-rays have to pass through overlying titanium layers of thickness $(n - 1/2)4200$ nm to reach the detector. The contributions from the 30 layers are added for the three-component radiations of the incident field to obtain total theoretical Ti k-X-ray intensity.

For calculating the intensity of iron k-X-rays, the implantation zone has been divided into six sublayers of thickness 21 nm each. The respective intensities of the three components of the incident radiation arriving at any layer are calculated as before. As before, only the photoelectric cross sections of the radiations arriving at any layer have been considered in calculating the Fe k-X-ray intensity. A fluorescence yield, $w_k = 0.342$ has been assumed for iron.^{3(d)} The Fe k-X-rays produced in the nth layer of the implantation zone have to pass through the overlying Fe-Ti mixture of thickness $= (n - 1/2)21$ nm to reach the detector. Contributions from the six layers are added to obtain total theoretical Fe k-X-ray intensity.

From the calculated intensities of Fe k-X-rays and Ti k-X-rays, R values have been determined for each level of Fe implantation dose. These

R values have been compared with the ratio of the total number of counts in $Ti(k_{\alpha} + k_{\beta})$ and $Fe(k_{\alpha} + k_{\beta})$ peaks for each target. It has been assumed that the detection efficiency of the Si(Li) detector for the titanium and iron X-rays is the same.

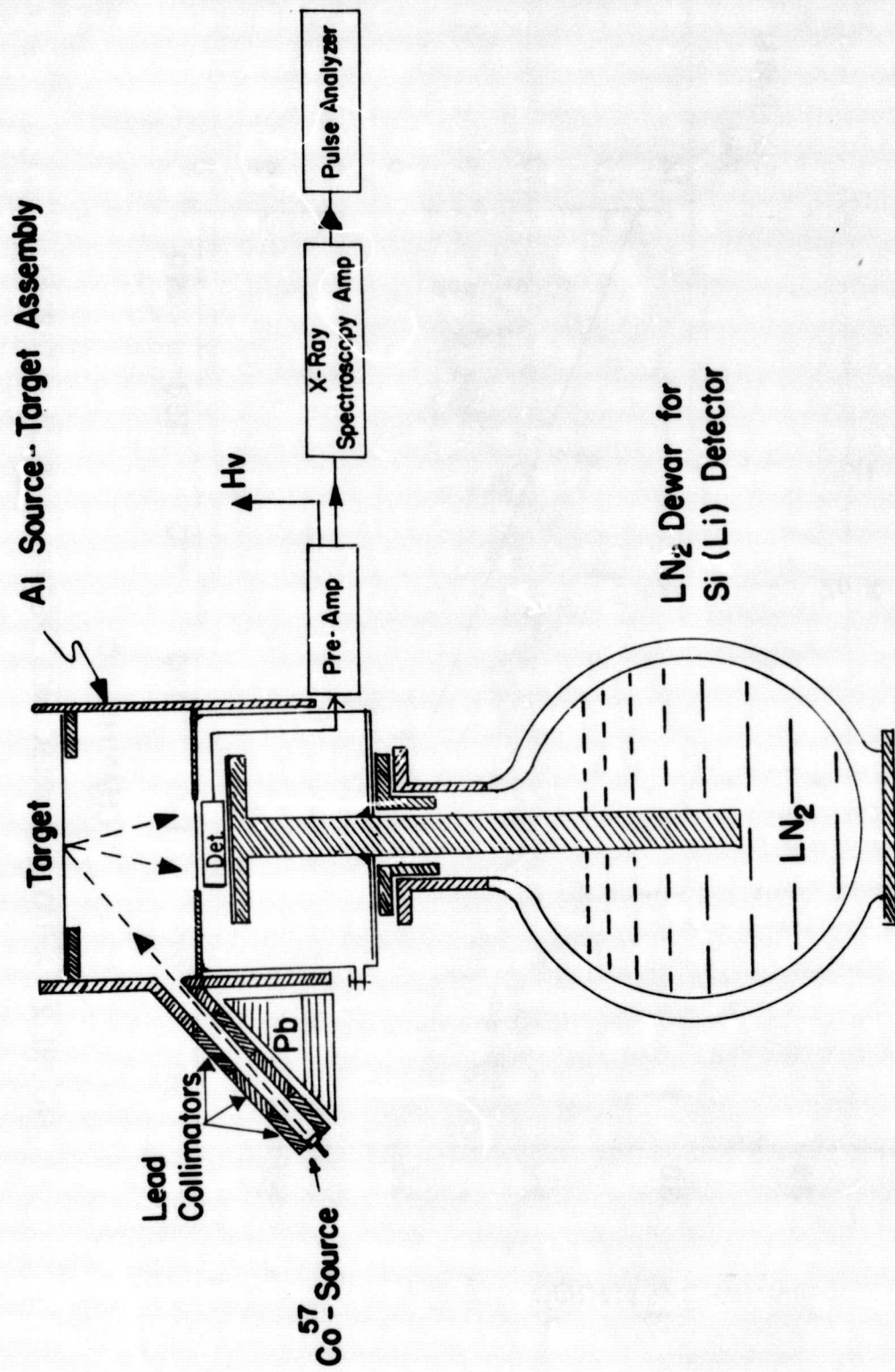


Fig. 1. Block Diagram of the Experimental Set-up for XRF System.

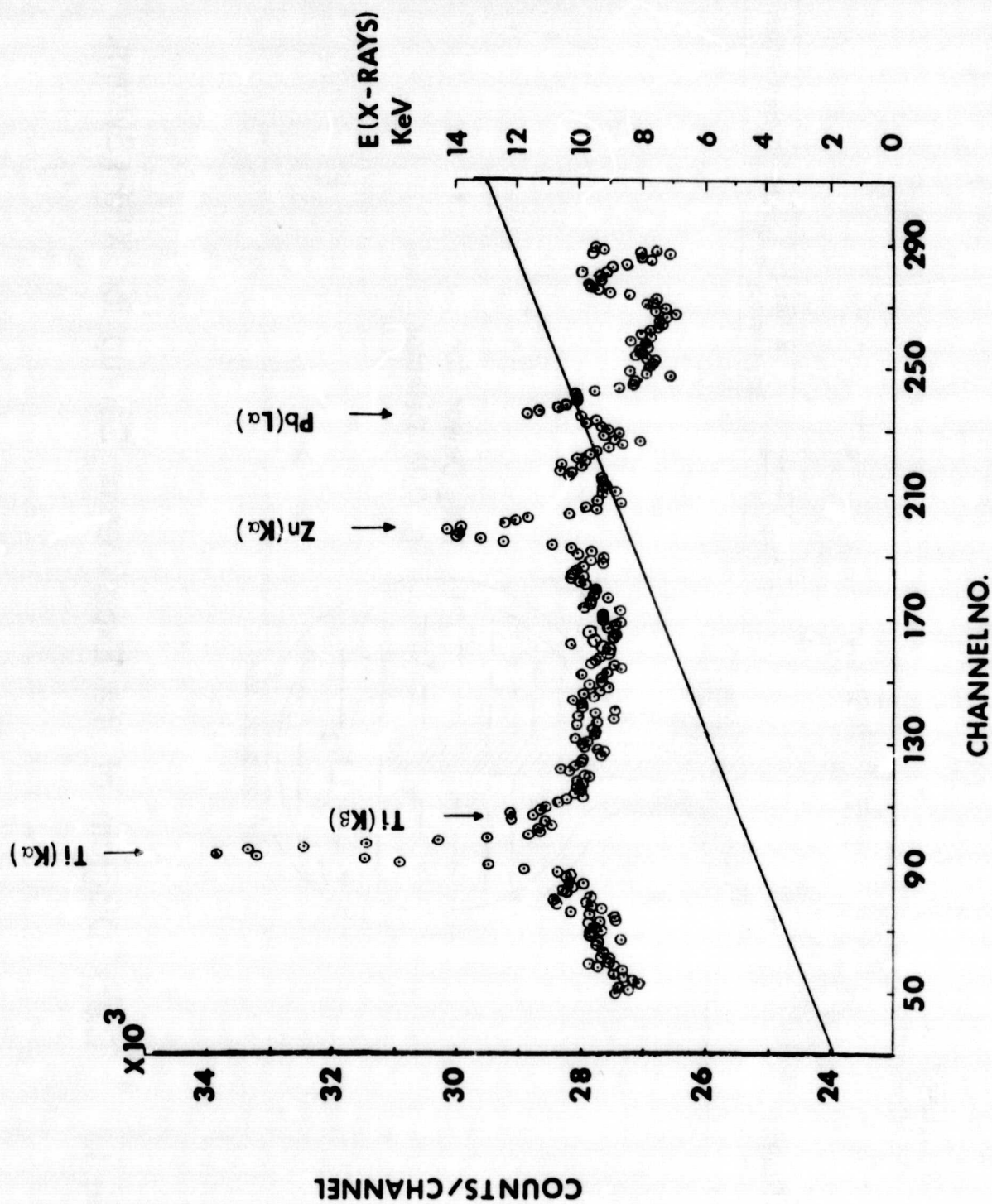


FIGURE 2. X-RAY FLUORESCENCE SPECTRUM FROM TI TARGET.

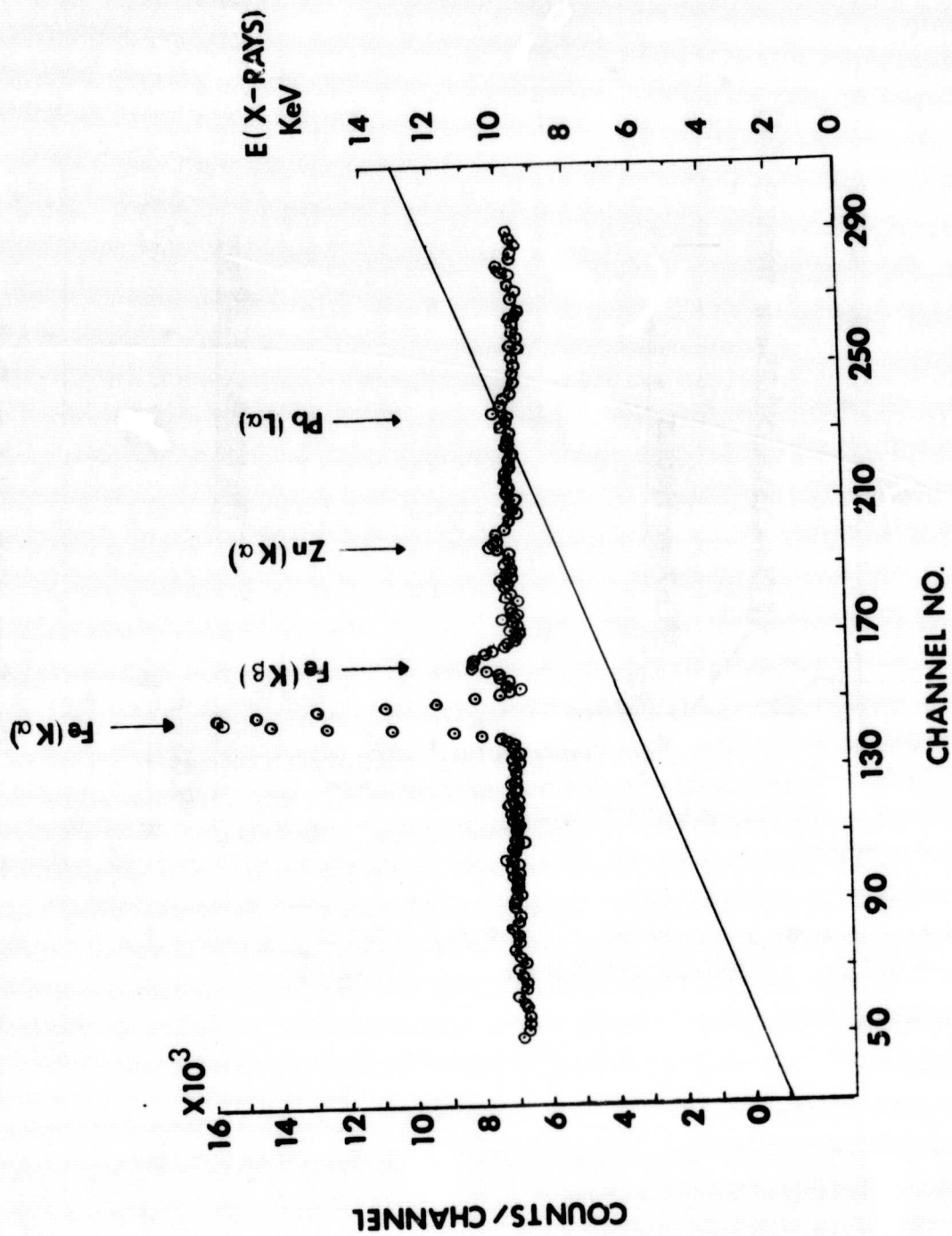


FIGURE 3. X-RAY FLUORESCENCE SPECTRUM FROM Fe TARGET.

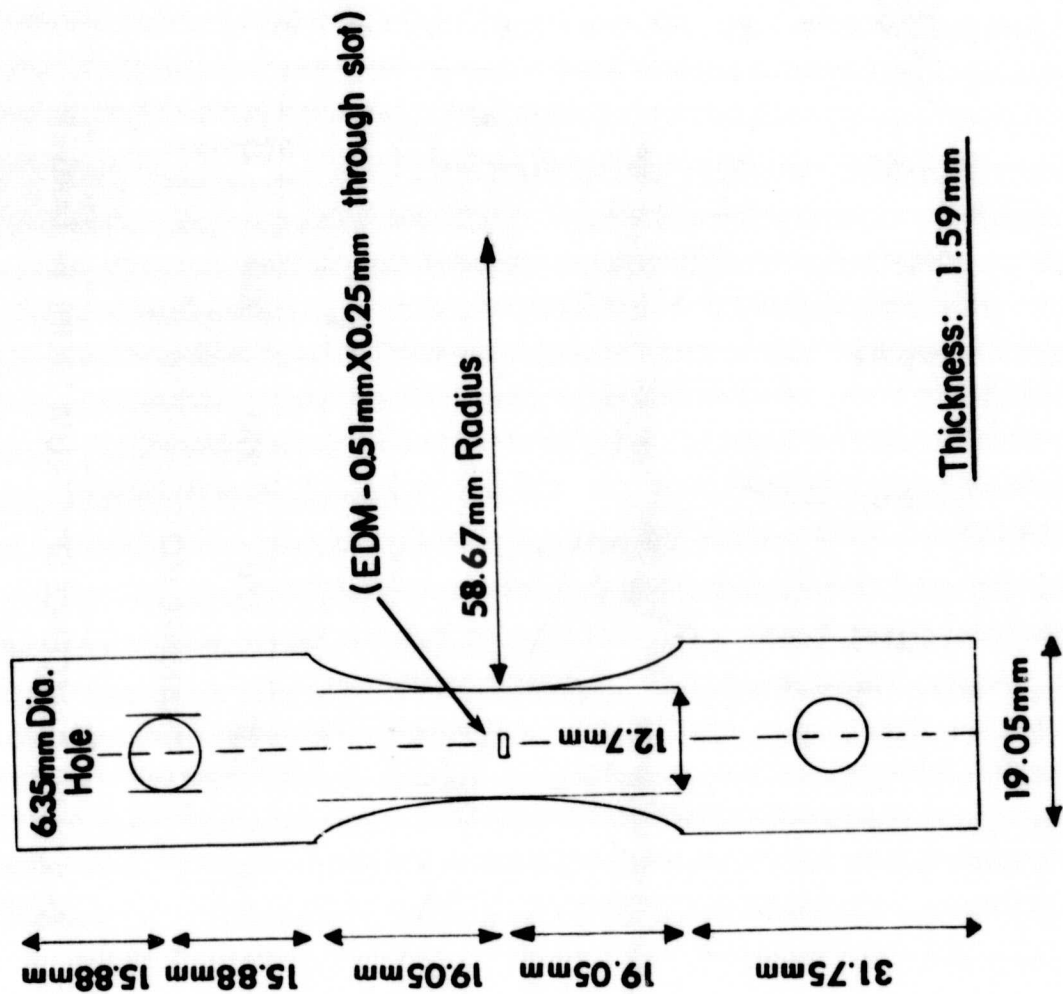


Fig. 4. Fe - Ti Fatigue Target Configuration - Not to Scale

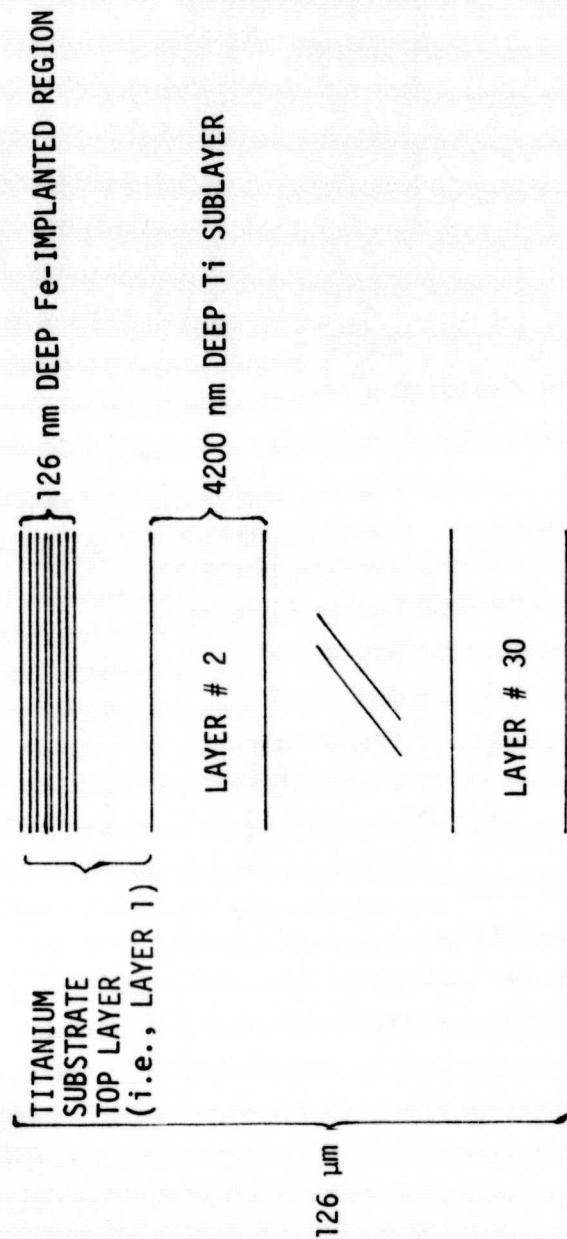


FIGURE 5.- CALCULATIONAL SCHEME FOR ATTENUATION SUFFERED BY Fe AND Ti
K-X-RAYS IN PASSING THROUGH THE OVERLYING MATERIAL.

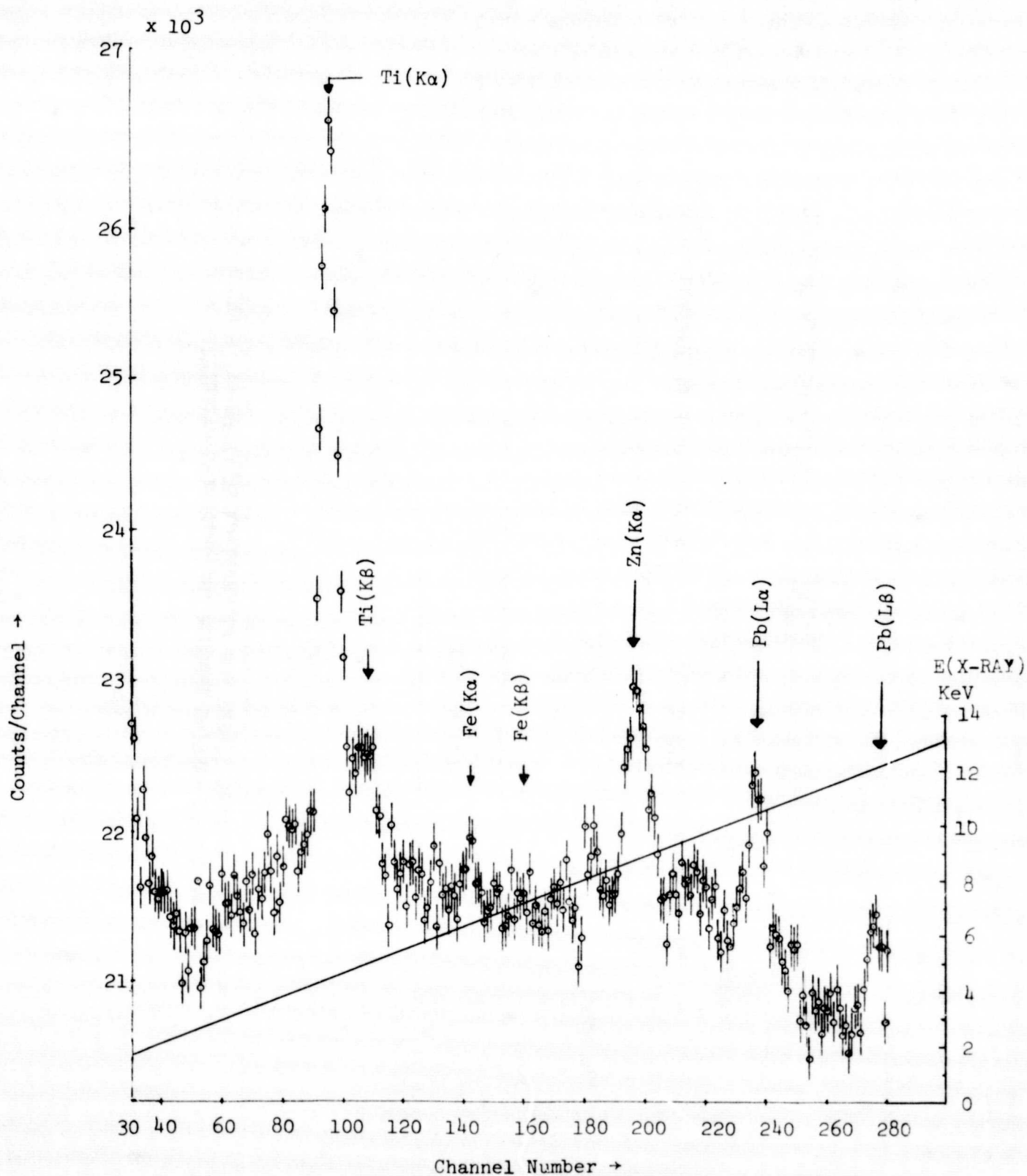


FIGURE 6 X-RAY FLOURESCENCE FROM Fe-Ti (80/o Fe) TARGET.

1. Report No. NASA TM 74062		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle An X-Ray Fluorescence System and Its Applications				5. Report Date	
				6. Performing Organization Code 1200	
7. Author(s) Jag J. Singh and K. S. Han				8. Performing Organization Report No.	
9. Performing Organization Name and Address Langley Research Center Hampton, VA, 23665				10. Work Unit No. 505-02-31-02	
				11. Contract or Grant No.	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, DC, 20546				13. Type of Report and Period Covered Technical Memorandum	
				14. Sponsoring Agency Code	
15. Supplementary Notes A radioisotope excitation X-ray fluorescence system has been developed and applied to determine the atomic fraction of iron implanted in titanium targets.					
16. Abstract We have developed an X-Ray Fluorescence (XRF) system based on a Co^{57} γ -ray source. The system has been used to calculate the atomic percentages of iron implanted in titanium targets. Measured relative intensities of Fe ($k_{\alpha} + k_{\beta}$) and Ti ($k_{\alpha} + k_{\beta}$) X-rays from the Fe-Ti targets are in good agreement with the calculated values based on photoelectric cross sections of Ti and Fe for the Co^{57} gamma rays.					
17. Key Words (Suggested by Author(s)) Radioactive Isotopes, Photoelectric Effect, X-Ray Fluorescence, Ion Implantation, Quantitative Analysis				18. Distribution Statement Unclassified - Unlimited	
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No of Pages 18	
				22. Price* \$3.50	